

SMALL ANGLE X-RAY SCATTERING STUDIES OF CARBON ANODES USED IN LITHIUM RECHARGEABLE BATTERIES

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ABSTRACT

In our laboratories, disordered carbons with predictable surface area and porosity properties have been prepared using inorganic templates containing well-defined pore sizes. The carbons have been tested in electrochemical cells as anodes in lithium secondary batteries. They deliver high specific capacity and display excellent performance in terms of the number of cycles run. *In situ* small angle X-ray scattering (SAXS) during electrochemical cycling was carried out at the Advanced Photon Source, at ANL. In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time. Results show that upon cycling the structure of the carbon remains unchanged, which is desirable in reversible systems. The fractal dimension and the invariant do not show significant variation upon cycling the templated carbon electrode. However, large variations were observed for the graphite electrode, indicating changes in the sample topology.

KEYWORDS: SAXS, carbon anodes, lithium secondary batteries

INTRODUCTION

Carbonaceous materials have received considerable interest for use as anodes ever since Sony introduced the lithium-ion battery [1,2]. Carbon containing systems are noted for potential safety and reliability advantages because the carbon anodes are less prone to form dendrites than metallic lithium anodes. Most investigations have utilized carbon materials that are available from existing sources such as natural graphite, cokes, carbon fibers, non-graphitizable carbon, and pyrolytic carbon [3,4]. In these studies, high lithium capacities have been found to be associated with either disorder [5] or the presence of hydrogen [6].

An alternative avenue is the custom synthesis of carbons specifically tailored for use as anodes in lithium-ion batteries. This latter approach provides predictable control over critical properties such as the surface area and the porosity. Previously, Sandf and coworkers employed pillared clays with known interplanar spacing as templates for the synthesis of custom carbon anode materials [7-9]. They have also recently found that carbons with curved lattices can exhibit enhanced lithium capacity over that of graphite [10].

Our latest approach focuses on the use of sepiolite clay to tailor the synthesis of carbonaceous materials. Sepiolite is a phyllosilicate clay insofar as it contains a continuous two-dimensional tetrahedral silicate sheet. However, it differs from other clays in that it lacks a continuous octahedral sheet structure. Instead, its structure can be considered to contain ribbons of 2:1 phyllosilicate structure, with each ribbon linked to the next by inversion of SiO_4 tetrahedra along a set of Si-O-Si bonds. In this framework, rectangular channels run parallel to the x-axis between opposing 2:1 ribbons, which results in a fibrous morphology with channels running parallel to the fiber length. Channels are $3.7 \times 10.6 \text{ \AA}$ in sepiolite (they are $3.7 \times 6.4 \text{ \AA}$ in palygorskite). Individual fibers generally range from about 100 \AA to 4-5 microns in length, $100\text{-}300 \text{ \AA}$ width, and $50\text{-}100 \text{ \AA}$ thickness. Inside the channels are protons, coordinated water, a small number of exchangeable cations, and zeolitic water. There are three sorption sites in sepiolite: (a) oxygen ions on the tetrahedral sheets, (b) a small amount of cation exchange sites ($0.1\text{-}0.15 \text{ meq}/100\text{gm}$), and (c) SiOH groups along the fiber axis. Adsorption is also influenced by the size, shape, and polarity of

the molecules involved. The SiOH groups act as neutral adsorption sites suitable for organic species. These factors are all important to our goal of loading the clay with certain organic monomers that will polymerize on the surface and, following a pyrolysis step, carbonize to a material suitable for use as a carbonaceous anode in secondary lithium batteries.

Our main objective is to synthesize carbon with pores sizes capable of Li^+ diffusion in a rechargeable battery. The carbonaceous materials are derived from ethylene or propylene upon incorporation in the vapor phase in the channels of sepiolite, taking advantage of the Brønsted acidity in the channels to polymerize olefins. In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time.

EXPERIMENTAL

Details about the synthesis of the carbonaceous materials can be found in reference [11]. In summary, ethylene and propylene (AGA, 99.95%) were loaded and pyrolyzed in the gas phase in one step. A three-zone furnace was used. Quartz boats containing sepiolite were placed within a quartz tube. The temperature of the oven was gradually increased from room temperature (about 5 °C/min) to 700 °C. The oven was then held at that target temperature for 4 hours. The clay from the loaded/pyrolyzed sepiolite sample was removed using HF. It was then rinsed to neutral pH and refluxed with concentrated HCl for 2 hours. The sample was washed with distilled water until the pH was > 5 to ensure that there was no acid left. The resultant carbon was oven dried overnight at 120 °C.

In situ small angle X-ray scattering (SAXS) during electrochemical cycling was carried out at the Advanced Photon Source, (Basic Energy Sciences Synchrotron Research Center CAT), Argonne National Laboratory. Monochromatic X-rays (8.8 keV), are scattered off the sample and collected on a 18 x 18 cm² position sensitive two-dimensional gas detector. The scattered intensity has been corrected for absorption and instrument background. The intensity has been expressed as a function of the scattering vector Q , which is defined as: $Q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength of the X-rays and θ is the scattering half angle. The value of Q is proportional to the inverse of the length scale (\AA^{-1}). The instrument was operated with a sample-to-detector distance of 68.5 cm to obtain data at $0.04 < Q < 0.7 \text{ \AA}^{-1}$. For these studies, a specially designed sample cell was used to record both the electrochemical response and SAXS data at the same time (see figure 1). The carbon sample was mixed with a teflon binder suspension (80/20 % w/w). The sample was oven dried and pressed against a Cu mesh. The electrode was then dried out in a vacuum oven at 80 °C overnight. A piece of lithium foil (0.008"; 0.203 mm from FMC Lithium Division, Gastonia, NC) with the same dimensions as the carbon composite was also pressed against Cu mesh. A propylene membrane (Hoechst-Celanese, Charlotte NC) was used as the separator. The electrodes were held together by using kapton tape along the edges. The electrolyte was 1 M LiPF_6 in a mixture of 50% v/v ethylcarbonate and 50 % v/v diethylcarbonate (Merck, Germany). A control experiment was performed using commercial graphite (Aldrich). The cell was discharged from the open circuit voltage (OCV) to 0 V and back to 2.5 V at a scan rate of 0.1 mV/s using a EG&G 273A potentiostat.

RESULTS AND DISCUSSION

In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time. The availability of very intense X-rays from synchrotron sources enables the use of SAXS to study the meso and micropore size distributions of many materials. Small-angle scattering from x-rays arises due to the presence of discontinuities in the density of a material. Thus, the particles and pores in the carbons can produce strong small angle scattering signals in a wide momentum-transfer range. The small angle scattering data can be modeled to obtain information on the microstructure of the porous network. In battery applications, if the liquid organic electrolyte penetrates the pores of the carbon anode, it leads to irreversible electrolyte decomposition during the first

electrochemical reaction of lithium with the carbon, and hence a large irreversible capacity. If the pores are small (of the order of 15 Å or less), and the structure remains intact, the liquid electrolyte cannot penetrate, so excellent reversible behavior should be expected.

Figure 2 shows a typical two-dimensional plot of the time-resolved studies of a lithium ion cell made with carbon derived from sepiolite/propylene composite (upper curves) and an electrode made from commercial graphite (bottom curves). A spectrum was taken of the cell at the open circuit voltage (OCV = 2.99 V for the templated carbon and 2.70 V for the graphite electrode) and used as the background correction for the subsequent measurements. Upon application of voltage, a spectrum was taken every 60 mV (every 5 minutes). The results obtained for the templated carbon indicated that during cycling, there are no structural changes upon lithium intercalation as is evidenced by the near overlap of all curves. This means that solvent penetration into the carbon anode, which causes irreversible capacity, is avoided and so excellent reversibility is attained. The results of the control experiment using commercial graphite clearly indicates that there are changes in the structure of graphite and that these changes are not reversible.

These curves can be analyzed to determine size of features, topology, and changes in total scattering. At small Q in the Guinier region, the radius of gyration (R_g), which is related to the size of the scattering features, can be determined. For example, R_g for spheres can be determined from the slope of $I(Q)$ vs Q^2 in a Q region where $R_g Q < 1.0$. Power law slope (fractal dimension) from the data is used to describe the topology of the system. Figure 3 shows the variation of the power law as a function of the applied voltage for both systems. For a layered material such as graphite a fractal dimension close to 2 is typical. When there is no lithium in the graphite lattice (at the OCV voltage), the fractal dimension must be close to the original material. In this case, the fractal dimension corresponded to 2.028, in excellent agreement to the theoretical value. As the voltage decreases, large fluctuations in the power law as a function of voltage are observed. At about 1.2 V, where the intercalation of lithium begins, the value of the power law increases to 2.16, indicating that the layers are expanding. These changes, however, are not reversible since the lattice does not contract to the original position. This is not the case for the templated carbon electrode, where the fractal dimension remains fairly constant throughout the voltage range. Since this is a disordered carbon, it is expected that the power law would be higher than graphite. The initial value corresponded to 2.57 and there are no significant changes throughout the measurement.

The invariant, Q_0 , is proportional to the square of the electron density difference in the system, and is calculated as follows:

$$Q_0 = \int_0^{\infty} I(Q) Q^2 dQ$$

Figure 4 shows a plot of invariant as a function of voltage for both electrodes. As expected, large variations in the electron density occur in the graphite electrode (especially at > 1.2 V) probably due to solvent incorporation upon irreversible lattice expansion, whereas the templated carbon shows variation within the statistical error.

CONCLUSIONS

Based on the electrochemical performance and much higher structural stability compared to graphite, carbon anodes derived from sepiolite as templates are demonstrated as good candidates for lithium ion cells. The synthetic approach described here yielded well defined carbon tubes with little or no graphitic character as evidenced by TEM. The yield of carbon based on the amount of inorganic template is about 25 times higher than our previous synthetic method, which makes it viable for commercial applications.

ACKNOWLEDGMENTS

This work has benefit from the use of the Advance Photon Source at Argonne National Laboratory, and was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract number W-31-109-ENG-38.

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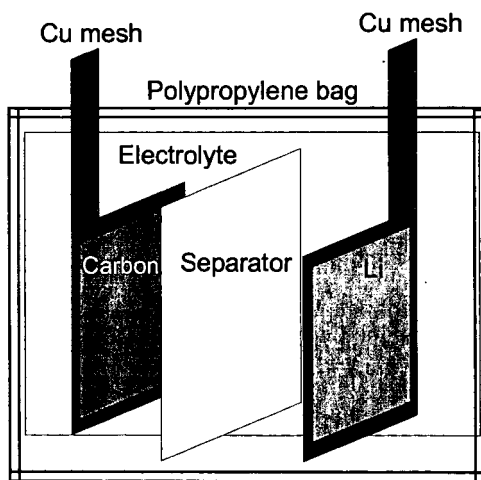


Figure 1: SAXS electrochemical cell for in situ measurements.

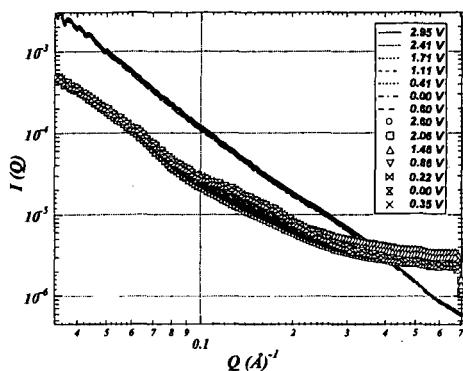


Figure 2: SAXS of electrodes made with templated carbon (upper lines) and commercial graphite (bottom symbols).

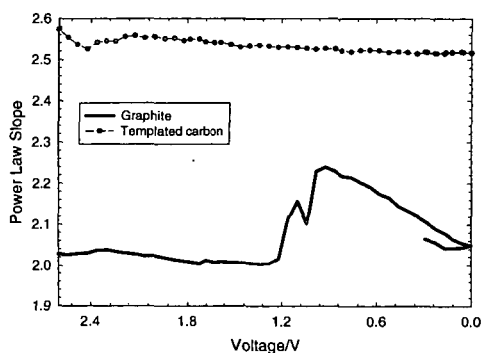


Figure 3: Variation of the power law as a function of discharged voltage of graphite and template electrodes.

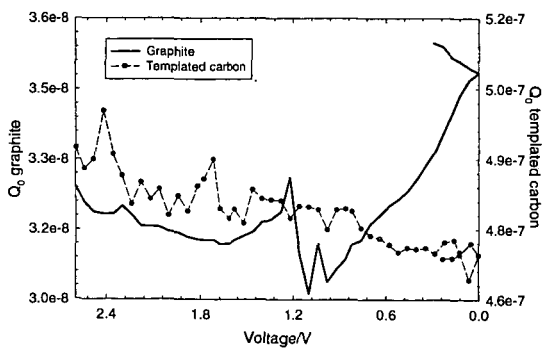


Figure 4: Invariant fluctuations as a function of discharge voltage of graphite and template electrodes.